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㉚ Process for isomerizing 1,1,2-trifluoro-1,2-dichloroethane to 1,1,1-trifluoro-2,2-dichloroethane.

㉛ 1,1,2-trifluoro-1,2-dichloroethane (A123a) is isomerized to 1,1,1-trifluoro-2,2-dichloroethane (A123) by contacting it with AlF₃ at temperatures ranging from 180° to 400° C. Advantageously, it is operated with mixtures of A123a with A123 and/or other chlorofluorocarbons coming from the preparation of A123 by hydrofluorination of perchloroethylene.

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The present invention generally relates to a process for isomerizing 1,1,2-trifluoro-1,2-dichloroethane (hereinafter referred to as A123a) to 1,1,1-trifluoro-2,2-dichloroethane (hereinafter referred to as A123). In particular it relates to the removal of A123a from its mixtures with A123 and optionally other chlorofluorocarbons by isomerizing A123a to A123.

5 The need for having available industrial processes for preparing A123 as free as possible from A123a has been recognized.

Such need is particularly recognized, for example, by the manufacturers of polyurethane foams, for the production of which A123 is used as foaming agent. In such case, the A123a contained therein decomposes and forms HCl, which corrodes the metal circuits of the plants.

10 The industrially most interesting processes for the preparation of A123 are based on the hydrofluorination of tetrachloroethylene in the gas phase, in the presence of proper catalysts.

Such a process is described for example in U.S. patent No. 4,766,260.

Such a preparation method always gives rise to A123a in amounts ranging from 5 to 20%, depending on the reaction conditions. Such product is difficult to be distilled-off from A123.

15 In principle it is possible to carry out the reaction under such conditions as to minimize the formation of A123a, for example by using high temperatures (about 360 °C); however, this is of little practical interest because under such conditions the process selectivity towards A123 is too low, while unacceptable amounts of by-products are obtained.

It is also possible to reduce the A123a content in the final reaction product by subjecting the mixture of 20 A123 and A123a to a treatment with anhydrous HF in the presence of the same catalyst as is used for its preparation, thereby obtaining the preferential fluorination of A123a to 1,1,1,2-tetrafluoro-2-chloroethane (A124).

However, the selectivity of such reaction is not high enough, wherefore also the fluorination of considerable amounts of A123 occurs.

25 The Applicant has now surprisingly found a process - constituting the object of the present invention - for converting A123a to A123 by contacting A123a, either alone or in admixture with A123 and/or other chlorofluorocarbons, in the gas phase, with a catalyst consisting of aluminium trifluoride (AlF_3), at temperatures ranging from 180 ° to 400 °C, but preferably from 220 ° to 320 °C.

The aluminium trifluoride utilized herein as a catalyst is generally present in the crystallographic forms

30 β , Δ and/or τ . However, little amounts of other crystalline forms are not harmful.

Said AlF_3 can be obtained by fluorination of alumina (Al_2O_3) with anhydrous HF or other fluorinating agents; or it can be prepared according to other methods of the art, such as, for example, the thermal decomposition of Na_3AlF_6 .

In the case of the fluorination of Al_2O_3 , the AlF_3 obtained has a surface area of 15-30 m²/g and granule sizes ranging from 20 to 200 microns (on the average: 80 microns).

The surface area of AlF_3 is not a critical element for the process of the invention, however, an AlF_3 having a high surface area, for example ranging from 15 to 30 m²/g, is preferred.

If such AlF_3 is obtained by fluorination of Al_2O_3 with anhydrous HF it is preferable, although not absolutely necessary, if at least 90% of the alumina contained therein is present in the fluorinated state.

40 The AlF_3 utilized as a catalyst in the process of the invention can be modified, in order to increase the activity thereof, by addition of little amounts - not exceeding 1% by weight calculated on the catalyst - of transition metals, preferably Fe, Ni, Co, Mn.

Preferably, the process of the invention is utilized for the isomerization of A123a in its mixtures mainly with A123 and optionally with other chlorofluorocarbons, which are obtained in the processes for the 45 fluorination of tetrachloroethylene with HF, in the gas phase.

In fact, the presence of products other than the isomers A123a and A123, for example A124 (CF_3CHClF), in the gaseous mixture obtained from such reaction does not prevent the isomerization of A123a. That is very advantageous in practice because it eliminates the necessity to carry out an accurate distillation of such products prior to the isomerization reaction. On the other hand, the fact that the reaction 50 mixture directly flows into the isomerization reactor does not sensibly modify the content of the products different from said isomers and present in the reaction mixture, which can be then recovered as such or recycled to the A123 production.

For the purposes of the process of the invention, the contact times of A123a with the catalyst are not particularly critical. Generally they are maintained from 5 to 100 seconds and preferably from 20 to 50 55 seconds.

Also the pressure does not exhibit particularly critical values; it can be the atmospheric pressure or a higher pressure.

The following examples are given merely to illustrate the invention, but not to limit the scope thereof.

Example 1

5 Into a tubular reactor made of Inconel 600^(R) having an inside diameter of 5 cm and a length of 80 cm, equipped with a porous bottom of sintered Inconel 600 and heated by means of heating elements, there were introduced 300 cc (340 g) of AlF₃ having a specific surface of about 20 m²/g. Such AlF₃ had been prepared by fluorination of Al₂O₃ with anhydrous HF till obtaining the fluorination of more than 90% of Al₂O₃.

The catalyst was treated with anhydrous HF at 250 °C for 2 hours in order to remove the moisture absorbed during the storing time.

10 About 100 g/h of a mixture containing 14.5 moles-% of A123a, 63.9 moles-% of A123 and 21.6 moles-% of other organic chlorofluorocarbons, mainly A124, were fed at a temperature of 240 °C.

The gases leaving the reactor were bubbled in water in order to remove acidity traces, were dried and condensed in a cold trap and then analyzed by means of gas chromatography (G.C.).

The results obtained are reported in Table 1A.

15 After a 60-65 hour run, the catalyst exhibited exhaustion phenomena, but the activity (expressed as the A123a fraction isomerized to A123) could be restored by raising the temperature to 270 °C without affecting the selectivity, expressed as ratio between fed A123 (sum of the isomers) and recovered A123, as shown in Table 1B.

20 By raising the temperature further on (Table 1C) it was possible to maintain the activity as the catalyst got exhausted, the selectivity losses being only negligible.

Lastly, by regenerating the catalyst by means of a treatment with air at 430 °C followed by refluorination with anhydrous HF at 300 °C, the original activity was fully restored (Table 1D).

Example 2

25 Into the same reactor of example 1, 300 cc of AlF₃ having the same characteristics as the one of example 1 were charged.

The reagent mixture was fed without subjecting the catalyst to any preliminary hydrofluorination treatment. By operating in like manner as in example 1, the results reported in Table 2 were obtained.

Example 3

30 Into the same reactor of example 1 there were charged 310 cc of the same AlF₃, which was treated for 3 hours at 400 °C with air and then was fluorinated for 2 hours at 400 °C with anhydrous HF.

35 By operating as in example 1, the results reported in Table 3 were obtained.

Example 4

40 Into the reactor of example 1 there were charged 310 cc of an aluminium fluoride containing 0.12% by weight of iron in the form of Fe₂O₃, which was treated for 2 hours at 300 °C with anhydrous HF.

By operating as in example 1, the results reported in Table 4 were obtained, wherfrom it is evident that the activity is much higher.

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TABLE 1A

Reaction temperature = 240 °C; t = 38"

	Feeding (Moles-%)	Operation hours						Obtained products (moles-%)			
		1.5	4	13	21	24.5	29.5	40	57.5	66	80
A123a	14.5	4.2	2.3	5.2	4.5	4.3	4.0	5.0	4.4	9.8	10.2
A123	63.9	75.8	75.6	73.3	74.4	74.9	75.0	74.1	75.0	69.1	68.8
Others	21.6	20.0	22.1	21.5	21.1	20.8	21.0	20.9	20.6	21.1	21.0

TABLE I B

Reaction temperature = 270°C; $\text{F} = 36^\circ\text{C}$

	Feeding (Moles-%)	Operation hours				
		88	91.5	103.5	107	111
		Obtained products (moles-%)				
A123a	14.5	2.3	1.8	1.9	3.4	4.5
A123	63.9	75.6	77.3	77.6	76.0	73.8
Others	21.6	22.1	20.9	20.5	20.6	21.7

TABLE 1C

Reaction temperature = 280°C — 320°C; (t = 36" - 33", respectively)

	Feeding (moles-%)	Operation hours						Obtained products (moles-%)		
		116	129	133	157	161	164	178	181	184
A123a	14.7	3.1	2.2	2.5	2.5	2.7	2.3	2.5	2.7	3.0
A123	65.9	76.8	77.7	77.4	77.3	77.5	77.0	76.5	76.3	79.6
Others	19.4	20.1	20.1	20.1	20.2	19.8	20.7	21.0	21.0	19.4

TABLE 1D

After regeneration - Reaction temperature = 280°C for tests not exceeding 11 operation hours, and 240°C for tests not exceeding 26 operation hours (t = 36" and 38", respectively)

	Feeding (moles-%)	Operation hours						Obtained products (moles-%)
		4	7	11	24	26		
A123a	10.6	0.3	0.2	0.2	5.0	2.3		
A123	65.4	72.1	72.8	74.2	73.1	75.6		
Others	24.0	27.6	27.0	25.6	21.9	22.1		

50 45 40 35 30 25 20 15 10 5

TABLE 2

Reaction temperature = 240°C for test not exceeding 11 operation hours; t = 38"
Reaction temperature = 280°C for the other tests; t = 36"

	Feeding (moles-%)	Operation hours							Obtained products (moles-%)		
		3	7.5	11	14	18	23	26	30	33	38
A123a	14.1	13.2	7.5	7.0	0.9	1.3	0.4	0.4	0.3	0.5	0.8
A123	70.2	71.6	78.0	78.0	85.0	85.1	85.2	85.4	84.6	84.3	84.2
Others	15.7	15.2	14.5	15.0	14.1	13.6	14.6	14.2	15.1	15.2	14.5

TABLE 3

Reaction temperature = 280°C for tests not exceeding 12 operation hours; t = 37"
Reaction temperature = 260°C for the other tests; t = 38"

	Feeding (moles-%)	Operation hours							Obtained products (moles-%)
		2	4.5	12	25	29			
A123a	10.6	0.2	0.2	0.2	0.6	0.3			
A123	65.4	73.2	75.6	74.8	79.0	72.7			
Others	24.0	26.6	24.2	25.0	20.4	27.0			

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TABLE 4

Reaction temperature = 260°C for tests not exceeding 7.5 operation hours; t = 38"

Reaction temperature = 240°C for tests not exceeding 13.5 operation hours; t = 40"

Reaction temperature = 220°C for the other two tests; t = 41"

	Feeding (moles-%)	Operation hours				
		3.5	7.5	9	13.5	16.5
A123a	14.1	0.6	0.1	0.6	0.6	0.3
A123	70.2	69.6	57.4	76.1	75.3	77.4
Others	15.7	29.2	42.5	23.7	24.1	22.3
						21.4

55 Claims

1. A process for isomerizing 1,1,2-trifluoro-1,2-dichloroethane to 1,1,1-trifluoro-2,2-dichloroethane, which consists in contacting 1,1,2-trifluoro-1,2-dichloroethane in the vapour phase with a catalyst composed

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of, or comprising AlF₃, at temperatures from 200° to 400° C.

2. The process of claim 1, wherein such temperature ranges from 220° to 320° C.
5. The process of claims 1 or 2, wherein the catalyst contains one or more transition metals selected from Fe, Mn, Co, Ni.
4. The process of claims 1 to 3, wherein 1,1,2-trifluoro-1,2-dichloroethane is in admixture with 1,1,1-trifluoro-2,2-dichloroethane.
- 10 5. The process of claims 1 to 4, wherein 1,1,2-trifluoro-1,2-dichloroethane is contained in the reaction mixture obtained in the preparation of 1,1,1-trifluoro-2,2-dichloroethane via hydrofluorination of perchloroethylene.

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I-35048 Stanghellina (Padova)(IT)

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DOCUMENTS CITED

Category Citation of document with reference to relevance

X EP-A-0 450 467 (DE)
* page 2, line 16
claims 1-8; examples

Y EP-A-0 282 005 (AU)
* claims; examples

X CHEMICAL ABSTRACTS,
7 May 1990, Columbi
abstract no. 17805-
SHINSUKE MORIKAWA :
hydrogen-containing
fluorohydrocarbons
page 680 ;
& JP-A-01 258 630 (16 October 1989
* abstract *

A EP-A-0 376 686 (E.I.)
* claims; examples

The present search report has been

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